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ASPECTS OF SYNTHESIS OF DECORITE OPACIFIED GLASS

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The paper presents data of the effect of the granular composition, the specific surface area of added metal powders, the batch preparation procedures, as well as the time/temperature conditions of synthesis, the type of the gas medium in the furnace, and the content interval and ratio of metallic additives on the color tone and the opacifying properties of glass melt produced.

Decorite is a decorative opacified glass variety imitating natural stones and based on the composition of industrially produced sheet glass with non-traditional metallic powder additives (RF Patent No. 1594883).

The synthesis of such glass has certain technological specifics, since the opacification is of mixed nature (liquation and crystallization) and is mainly related to the sulfidizing process.

The reaction of sulfidizing in the general form can be represented as follows:

$$SO_4^{2-} + Me \rightarrow S^{2-} + MeO;$$

$$S^{2-} + Me_1O \rightarrow Me_1S + O_2\uparrow.$$

The formation of sulfides in the melt and their quantity depends on the nature of the sulfidized metal, the time/temperature conditions of synthesis, the composition of the gas atmosphere in the furnace, as well as the redox potential of the glass melt. The metals which are less strongly bonded to oxygen but have great chemical affinity to sulfur will be the first to sulfidize. Based on their increasing chemical affinity to sulfur, the metals can be arranged in the following series [1]: Cu < Co < Fe < Cd < Zn < Mg < Ca.

The presence of a reducing agent is favorable for the reactions of metals (oxides, silicates) with a sulfidizing agent and the formation of sulfides. With an increasing redox potential of the batch, the sulfide level of the melt increases (Fig. 1), the starting temperature of sulfide formation decreases, and the yield of sulfide grows (Fig. 2) [1 – 4].

In practical glass melting, carbothermal reduction is widely used for sulfide pigmentation [5, 6]. However, upon adding carbon in the unfixed (graphite, coke, anthracite) or chemically fixed form (flour, sugar, sawdust) to the batch, one is confronted with intense formation of secondary gas bubbles in the glass melt, excessive consumption of the pigments and the reducing agent, and fluctuations in the intensity of the glass melt tint. Therefore, it is advisable to select a reducing agent whose excessive amount could be released from the glass melt at high temperatures, for instance, as the result of pyrolysis, sublimation, or evaporation, or could become chemically fixed with other glass components.

In metallurgy, aluminothermal reduction [7, 8] is used in refining and preparation of ferroalloys containing reducing forms of Ti, V, Nb, Zr, W, Mo, Cr, Mn, Fe, Ni oxides, etc., which in general form can be represented as follows:

$$\frac{2}{m} Me_nO_m + \frac{4}{3} Al \leftrightarrow 2\frac{n}{m} Me + \frac{2}{3} Al_2O_3.$$

Metallic aluminum is a gray-white metal with melting point 933.1 K, boiling temperature about 2600 K, and density 2700 kg/m^3. It is characterized by high chemical activity at elevated temperatures.

A substantial advantage of aluminothermal reduction is the exothermic type of reaction, since the oxidation of aluminum is accompanied with a substantial heat release (1584 kJ/mole), which is significantly more than in oxidation of other metals. Furthermore, aluminum oxide is one of the components of industrial glass compositions. Its presence (up to 6 wt.%) enhances the chemical stability and improves the mechanical and thermal strength of glass [9].

Based on analysis of patents and technical literature and summarizing the results of laboratory research, the authors selected metallic aluminum as a non-traditional reducing additive, since it facilitates intense reactions between the batch components, generally intensifies the glass melting process, and creates favorable thermodynamic conditions for the formation of sulfide.

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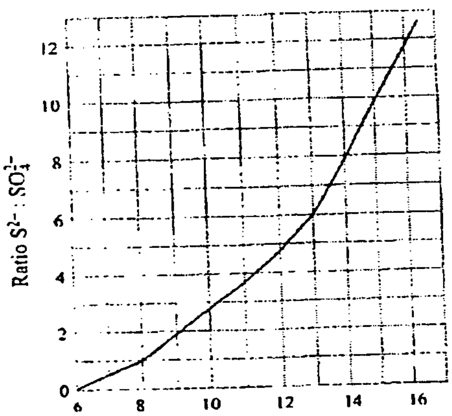

Fig. 1. Variation of the sulfide level of melt depending on the content of the reducing agent in the batch.

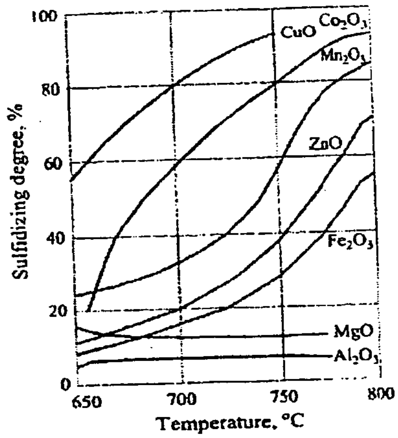

Fig. 2. Temperature dependence of the degree of sulfidizing of metal oxides (the content of reducing agent in the initial batch is 30%).

However, glass melt is known to be an aggressive medium. Two oxidizers (hydrogen ions and dissolved oxygen), the alkaline medium, and the effect of high temperatures will lead to the oxidation of metallic aluminum, i.e., will significantly decrease its activity.

A method for the protection of metals from corrosion is known in practical metallurgy, in which a doping additive is introduced into the melt, whose purpose is to distract to itself the action of the aggressive medium while preserving and extending the reactivity of the protected metal [10, 11].

In selecting such metal, the authors were guided by the fact that Decorite belongs to thermosensitive sulfide-zinc glasses whose decorative and opacifying properties are related to the presence of sulfurous iron and zinc compounds in the glass melt. The tint brightness, the degree of clarity, and the type of color ornamentation depend on the quantity and ratio of these compounds [5, 12].

Metallic zinc is a dark gray heavy metal of density 7140 kg/m^3. Its melting point is 692.5 K, and the boiling temperature is 1180 K. It becomes oxidized by air oxygen when heated over 498 K, and under intense heating, it ignites and burns with a bright blue-green flame forming an oxide:

$$Zn + \frac{1}{2}O_2 \leftrightarrow ZnO + 312.12 \text{ kJ/mole.}$$

In using powdered metallic zinc as the protective dopant and the main zinc-bearing material in the synthesis of Decorite glass, a number of problems can be simultaneously solved :

– the reducing activity of metallic aluminum is preserved, thus increasing the sulfide level of the melt;

– zinc oxidation is an exothermic process, which intensifies the reactions between the batch components and the glass melting process;

– having increased affinity to sulfur, zinc existing in the active (metallic) form retains the sulfide sulfur in the glass melt, preventing it from volatilization and oxidation, and binds it in the $[ZnS_4]$ tetrahedron, which is capable of replacing SiO_4 in the vitreous lattice or forming zinc sulfide ZnS, which later under specific temperatures produces an intricate marble-like pattern;

– ZnS oxidized to ZnO also reacts with sulfide sulfur forming a strong bond and in part is integrated in the glass composition in the form of ZnO, thus improving the melting and working properties of the glass melt [1, 3, 7, 13, 14].

Based on the performed studies, metallic aluminum and zinc powders were used for the synthesis of decorative glasses. Special attention in the synthesis of glasses based on metallic powders was paid to the granulometric composition of the latter, as well as the sequence of feeding and mixing of metals in the course of batch preparation.

The present study describes the results of studying the effect of the granulometric composition, the specific surface area of introduced metals, the batch preparation conditions, the time/temperature conditions of synthesis, and the limiting quantitative ratios of introduced metals (aluminum and zinc) on the degree of opacification and the color tone of the resulting glass melt. The studies were carried out using aluminum metallic powder of grades A and B, which differ significantly in their granulometric compositions.

It is known [14] that the inertness of metallic aluminum powder with respect to water and moist air under normal conditions is due to the presence of the oxide film on its surface:

$$2Al + 1.5O_2 \leftrightarrow Al_2O_3 + 1584.5 \text{ kJ/mole.}$$

The specified film is of small thickness but of high density, and it reliably protects the metallic powder from further oxidation. However, this protective layer is not resistant to

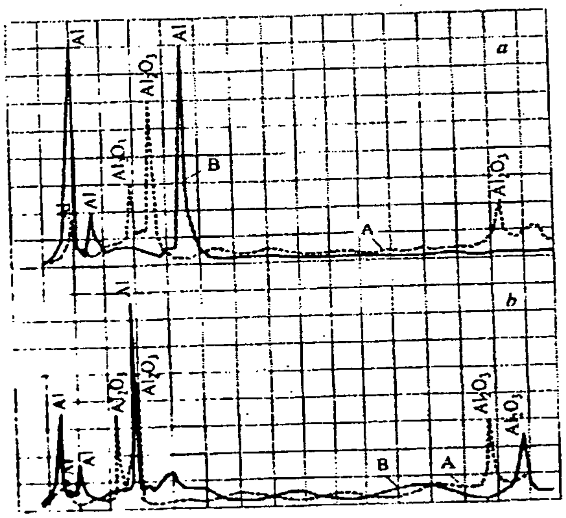

Fig. 3. X-ray patterns of the products of reaction of aluminum metal powders of grades A and B with alkaline medium in batch exposed for 1 h (*a*) and 24 h (*b*).

the effect of alkalis, and increased temperatures intensify this process, due to the increased diffusion mobility of the particles. As a result, the next layer of the metal becomes oxidized, and the more developed the surface, the sooner an oxide film whose thickness is equivalent to a few crystal lattice elements is formed. In due course, the oxide seeds capture the entire metal surface and convert active metal into a continuous oxide layer [10].

The reducing capacity of powders was investigated in batches of varying moisture levels prepared in industrial conditions. The initial materials were quartz sand, dolomite, chalk, pegmatite, soda ash, and sodium sulfate. A mixture of aluminum and zinc metal powders was either added to the ready moistened batch (procedure 2) or introduced directly in the course of batch preparation (procedure 1). The redox potential (ROP) of the batch was determined based on the method described in [15]. The investigation was performed using the industrial sheet glass composition.

In the case of using finely dispersed grade A aluminum powder, the amount of heat released in destroying the protective layer and in further oxidation of metal was so substantial that the metallic particles became luminescent, and the entire batch volume was heated to 403 K.

In using coarser-grained aluminum powder of grade B with a not very large specific surface area of the particles, the released oxidation heat was absorbed by the volume of the metal particles; therefore, no significant increase in the batch temperature took place, and metallic aluminum, due to the emerging protective film, maintained its reactivity as a most active reducing agent and melting catalyst.

The x-ray patterns of the batches (Fig. 3) exposed for 1 h and 24 h confirm the fact that virtually all metallic powder of grade A transformed into aluminum oxide after 1 h, whereas powder of grade B remained an active metal even after 24 h.

Table 1 shows the ROP of the batches depending on the grade of metallic aluminum powder used, the batch moisture, and the batch preparation procedure.

Thus, metallic powder of grade B provides for highly reducing conditions.

The effect of the time/temperature conditions of synthesis, the type of the gas atmosphere in the melting tank, and the interval of metal additives (aluminum and zinc) content and ratio on the color tone and the opacifying properties of the produced glass melt were studied on industrially prepared batches of varying moisture levels based on grade B aluminum powder and procedure 2 of batch preparation.

The batches were melted in industrial conditions in a gas-flame batch furnace of capacity 600 kg with the maximum melting temperature 1450 – 1480°C. The evaluation criteria were based on the initial clear glass and its capacity for opacification under additional heat treatment. The results of the analysis of experimental glasses determining the content of sulfide and sulfate sulfur, as well as of zinc oxide, are shown in Table 2.

The following was established:

– the batch moisture should be within the limits of 3 – 4%, since with a lower moisture level, the content of sulfide sulfur decreases due to volatilization, and with a higher moisture level, sulfur is transformed from the sulfide form to the sulfate form;

– neither batch moisture, nor the conditions of batch preparation have a significant effect on the content of zinc oxide in glass;

– depending on the quantity of Fe_2O_3 (0.1 – 0.5%) in the glass, the interval of the introduced metallic powder content is 0.45 – 10.00% per 100% glass melt, with the Zn : Al ratio ranging from 2 : 1 to 4 : 1.

TABLE 1

Metallic aluminum powder	Batch preparation procedure	Batch moisture, %	Batch ROP
Grade A, fine-dispersed	1	3	– 10
		4	– 12
	2	3	– 16
		4	– 26
Grade B, coarse-dispersed	1	3	– 130
		4	– 142
	2	3	– 158
		4	– 160

TABLE 2

Batch moisture	Mass content in glass, %		
	S^{2-}	SO_3	ZnO
2	0.09	0.24	1.40
3	0.11	0.27	1.39
4	0.12	0.34	1.42
5	0.10	0.34	1.40
7	0.06	0.37	1.36

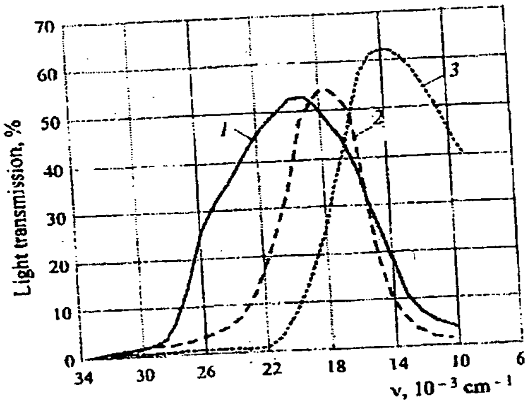

Fig. 4. Spectral characteristics of glasses synthesized in highly reducing (*1*), highly oxidizing (*2*), and weakly reducing/neutral (*3*) conditions.

The most intense opacification of the whole glass volume in the entire working temperature interval is observed in the interval of the specified ratio of metals.

The glass should be synthesized under moderately reducing/neutral conditions with a maximum temperature 1420 – 1450°C and with a minimum exposure in the high temperature region.

At a high rate of temperature rise and at high melting temperatures (1450 – 1480°C), the glass melt color is quickly saturated and changes from amber to dark brown, almost black. With a long exposure in the maximum temperature region, sulfide sulfur is partly burned out, especially in the surface layers, and the glass melt becomes saturated with a high number of secondary gas bubbles, whereas the degree of opacification is abruptly decreased.

Under highly reducing conditions of synthesis, the glass color becomes green-sky-blue as the consequence of reduced iron (FeO) pigmentation and the decolorization by zinc oxide. Under highly oxidizing conditions, the glass melt color tone varies to brownish-green due to the oxidation of sulfide sulfur to the sulfate form and the emergence of yellow color centers produced by Fe_2O_3 (Fig. 4).

Thus, the performed studies substantiated the expediency of selecting metallic aluminum and zinc powders as non-traditional additives in the production of opacified Decorite glass.

Metallic aluminum develops the favorable thermodynamic conditions for sulfide formation and creates the marble-like opacification effect, whereas zinc preserves the sulfide level in the melt, as it retains and binds sulfide sulfur contained in the melt in a strong bond and forms zinc oxide. The granular composition and the specific surface area of metallic aluminum powder have a significant effect on the opacifying properties of the glass melt.

Decorite glass is intended for highly efficient production lines (float glass, rolling), but can be successfully used as well in the production of glass containers and household glass.

REFERENCES

1. D. N. Klushin, *Sulfidizing of Nonferrous Metals* [in Russian], Metallurgiya, Moscow (1968).
2. I. A. Novokhvatskii, *Gases in Oxide Melts* [in Russian], Metallurgiya, Moscow (1975).
3. É. K. Lukashenko, A. M. Pogodaev, and I. A. Sladkova, *Collected Problems of Theory of Nonferrous Metallurgy Processes* [in Russian], Metallurgiya, Moscow (1971).
4. B. V. Nekrasov, *Fundamentals of General Chemistry* [in Russian], Khimiya, Moscow (1973).
5. I. Kotsik, I. Nebrzhenskii, and I. Fanderlik, *Tinting of Glass* [Russian translation], Khimiya, Moscow (1983).
6. Z. Karch, "Prispevek k chemickemu vyzkumu podstaty a mechanismu hnedeho zabarvent skts," *Sklar Keram.*, 17(8), 247 – 249 (1967).
7. M. Kh. Karapet'yants, *Introduction to the Theory of Chemical Processes* [in Russian], Vysshaya Shkola, Moscow (1975).
8. Yu. A. Pliper and G. F. Ignatenko, *Reduction of Metal Oxides Using Aluminum* [in Russian], Metallurgiya, Moscow (1967).
9. V. V. Pollyak, P. D. Sarkisov, V. F. Solinov, and M. A. Tsaritsyn, *Technology of Building and Engineering Glass and Slag Glass Ceramics* [in Russian], Stroiizdat, Moscow (1983).
10. V. V. Scorchelletti, *Theoretical Principles of Corrosion of Metals* [Russian translation], Khimiya, Leningrad (1973).
11. D. N. Klushin, P. D. Reznik, and S. I. Sobol', *Use of Oxygen in Nonferrous Metallurgy* [in Russian], Metallurgiya, Moscow (1973).
12. E. G. Rachuk, *Soviet Sulfide-Zinc Glass* [in Russian], Legkaya Industriya, Moscow (1975).
13. M. M. Lakernik, *Electrothermics in Metallurgy of Copper, Lead, and Zinc* [in Russian], Metallurgiya, Moscow (1967).
14. L. I. Martynenko and V. I. Spitsin, *Selected Chapters of Inorganic Chemistry. A Manual, Issue 2* [in Russian], Izd. MGU, Moscow (1968).
15. Yu. A. Guloyan, G. V. Kochetkov, and I. V. Tsokurenko, "On estimation of the reducing potential of container glass batches," in: *Production and Studies of Glass and Silicate Materials, Issue 8* [in Russian], Yaroslavl (1985), pp. 12 – 14.